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A. APPARENT POPULATION TEMPERATURES
FOR OH IN FLAMES. II. EMISSION STUDIES

B. APPARENT POPULATION TEMPERATURES
FOR QH IN FLAMES. III. ABSORPTION STUDIES

C. APPARENT POPULATION TEMPERATURES
FOR OH IN FLAMES. IV. ISOINTENSITY
METHOD FOR EMISSION EXPERIMENTS

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Even if a Boltzmann distribution exists for the population of molecules in various energy levels, it is not possible to obtain a satisfactory interpretation of experimental data unless the product of maximum spectral absorption coefficient P_{\max} and optical density X is sufficiently small. Detailed calculations are presented which show that the experimental results, which suggest anomalous rotational temperatures for $2 \Sigma \rightarrow 2 \Pi$ transitions of OH and weak predissociation for the higher rotational energy levels, can be accounted for by using sufficiently large values for $P_{\max} X$. In this connection it is of interest to note that the large values of $P_{\max} X$ are in agreement with the best available absolute intensity estimates based on data which have been obtained by Oldenberg and his collaborators. Plots for the determination of population temperatures for an isothermal emitting system at 3000°K are summarized for the P_1 - and P_2 - branches of the (0,0)- band of OH for $2 \Sigma \rightarrow 2 \Pi$ transitions. Apparent population temperatures up to 19,000°K can be obtained. Particularly noteworthy is a falling off in intensity for the higher rotational energy levels, which can be seen to represent a natural consequence of the fact that the maximum spectral emissivity decreases rapidly with increasing rotational energy of the initial state. We believe that the calculations given in this article cast doubt upon the significance of reported rotational flame temperature anomalies concerning OH.

I. INTRODUCTION

Experimental studies of population temperatures in flames have been reported, by different investigators, for the $2 \Sigma \rightarrow 2 \Pi$ transitions in flames at low pressures^{1,2} and at atmospheric pressures.^{1,3,4} When the experimental data are treated according to conventional techniques, the plots which are used for the determination of rotational temperatures are found to

* Supported by the O.N.R. under contract Nonr-220(03), NR 015 210.

[†] The author is indebted to Mr. E. K. Björnerud for performing the numerical calculations.

¹ A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. 208A, 63 (1951) and earlier publications.

² S. S. Penner, M. Gilbert, and D. Weber, J. Chem. Phys. (In press).

³ H. P. Bröida and K. E. Shuler, J. Chem. Phys. 20, 168 (1952).

⁴ H. P. Bröida, J. Chem. Phys. 19, 1383 (1951).

exhibit discontinuities or curvatures both in the regions of small and large values of the rotational energy $E(K)$ of the initial (upper) state. The "discontinuities" observed for small values of K have been variously attributed to the formation of OH in the excited electronic state by different chemical reactions leading to a bimodal distribution of population densities,^{1,4} to falsification of experimental data by absorption of emitted radiation by cooler gas layers through which the flame is viewed,⁴ and to self-absorption.⁵ The curvatures observed for large values of K have been interpreted¹ to indicate predissociation according to the process



In a previous publication⁵ we have called attention to the fact that the best available intensity estimates⁷ on OH indicate that the product of the maximum absorption coefficient P_{\max} and of the optical density of the emitters X is generally larger than unity for the more intense spectral lines of OH in flames. In Section II we examine quantitatively the effect of the size of $P_{\max} X$ on apparent population temperatures in flames for emission experiments. This study leads us to the conclusion that most of the experimental data can be accounted for by a population temperature which is close to the adiabatic flame temperature. Thus, we are in substantial agreement with Dieke that the observed discontinuities or curvature for small values of E_K may be the result of self-absorption.* Furthermore, it is not certain that the apparent falling

⁵ G. H. Dieke and H. M. Crosswhite, The Ultraviolet Bands of OH, The Johns Hopkins University, Bumblebee Series Report No. 87, 1948.

⁶ S. S. Penner, J. Chem. Phys. (in press). Hereafter referred to as I.

⁷ R. J. Dwyer and O. Oldenberg, J. Chem. Phys. 12, 351 (1944); O. Oldenberg and F. F. Rieke, J. Chem. Phys. 6, 439 (1938).

* The term self-absorption is somewhat misleading since it suggests that the basic law for emission or absorption of radiation shows that intensities vary linearly with optical density which is, of course, not the case.

off in intensity for large values of E_x , for which Gaydon and Wolfhard have invented an ingenious predissociation mechanism, is not also the result of falsification of experimental data by self-absorption.

II. THE EFFECT OF SELF-ABSORPTION ON APPARENT POPULATION TEMPERATURES IN EMISSION EXPERIMENTS

The effect of instrumental distortion on experimental data will be neglected in the present discussion. For the sake of simplicity, a complete analysis will be carried out only for studies involving peak intensities. It is shown in Appendix I that the results obtained for integrated intensities, for representative calculations, are similar to those obtained for peak intensities.* Hence the applicability of the principal conclusions reached in the following discussion depends only on the experimental determination of valid relative peak or integrated intensities for different spectral lines.

A. Equations for the Determination of Apparent Population Temperatures

For spectral lines with Doppler contour the maximum observable intensity in emission, I_{\max} , is given by the relation

$$I_{\max} = R^0(\nu_{\ell u}) \left[1 - \exp(-P_{\max} I) \right] \quad (1)$$

where $R^0(\nu_{\ell u})$ denotes the intensity of radiation emitted by a blackbody, which is at the same temperature T_u as the gaseous emitters under study. The

* In general, peak intensity ratios are obtained if the instrumental slit width is small compared to the line-width, whereas total intensity ratios are measured when the instrumental slit-width is large compared to the line-width.

frequency $\nu_{\ell u}$ is obtained from the values of the upper (E_u) and lower (E_ℓ) energy levels by use of the Bohr frequency relation. For spectral lines with Doppler contour it is well-known that $P_{\max} = S_{\ell u} (mc^2/2\pi k T_t \nu_{\ell u}^2)^{\frac{1}{2}}$, where $S_{\ell u}$ is the integrated intensity for the transition under study, m equals the mass of the radiator, c is the velocity of light, k represents the Boltzmann constant, and T_t is the translational temperature (I). Let

$$\xi' = I_{\max}/R^0(\nu_{\ell u}) \quad (2)$$

and

$$x = -P_{\max} X \quad (3)$$

whence it follows that

$$-\xi' = \sum_{n=1}^{\infty} x^n/n! \quad (4)$$

It is evident that ξ' represents the maximum value of the spectral emissivity for the emitting spectral lines. If the population temperature of the emitter is defined in the usual way, then $\xi' \leq 1$.

By using Eq. (1) and the defining relations for ξ' and x it is readily shown that

$$-x = \xi' \left[1 + \frac{1}{2} \xi' + (1/3) (\xi')^2 + (1/4) (\xi')^3 + \dots \right] \quad (5)$$

For very small values of ξ' , Eq. (5) leads to the usual result, viz., $-x = \xi'$ or $(S_{\ell u} X) (mc^2/2\pi k T_t \nu_{\ell u}^2)^{\frac{1}{2}} = I_{\max}/R^0(\nu_{\ell u})$ for $\xi' \ll 1$. (6)

From an appropriate expression for $S_{\ell u}$ and Eq. (6), it is readily shown that (I)

$$\frac{\partial \ln [I_{\max}/(\nu_{\ell u})^3 g_u (q_{\ell u})^2]}{\partial E_u} = - \frac{1}{k T_u} \quad \text{for } \xi' \ll 1 \quad (7)$$

where g_u is the statistical weight of the upper (initial) energy state and $q_{\ell u}$ is the matrix element for the transition under study.

If ξ' is not small compared to unity then it is no longer possible to obtain the value of T_u in a simple manner unless absolute values of ξ' are

available. Thus, in general,

$$\frac{\partial \ln \left\{ I_{\max} \left[1 + \frac{1}{2} \xi' + (1/3)(\xi')^2 + (1/4)(\xi')^3 + \dots \right] / (v_{\ell u})^3 g_u(q_{\ell u})^2 \right\}}{\partial E_u} = -\frac{1}{kT_u}. \quad (8)$$

B. A Method for Demonstrating the Effect of Self-Absorption on Apparent Population Temperatures of OH ($^2\Sigma \rightarrow ^2\Pi$ Transitions).

We proceed now to examine quantitatively the effect of the absolute values of ξ' on apparent population temperatures determined according to Eq. (7). In particular, it will be demonstrated that for small values of K the experimentally observed curvatures and discontinuities can be accounted for quantitatively by a uniform temperature T_u which agrees closely with the adiabatic flame temperature.

Plots of $\log [I_{\max}/(v_{\ell u})^3 g_u(q_{\ell u})^2]$ as a function of E_u can be constructed for various assumed values of ξ' by proceeding according to the scheme outlined below.

(1) Assume a value of ξ' , for example, for the P_1 -branch, (0,0)-band, for the transition identified by the index $K=1$, using the notation of Dieke and Crosswhite.⁵ It is then evident from Eqs. (1) and (2) that

$$(P_{\max} X)_{K=1} = -2.303 \log [1 - \xi'(K=1)]. \quad (9)$$

(2) Calculate the ratio $S_{\ell u}(K)/S_{\ell u}(K=1)$ from the expression

$$\frac{S_{\ell u}(K)}{S_{\ell u}(K=1)} = \frac{g_u(K)}{g_u(K=1)} \frac{[q_{\ell u}(K)]^2}{[q_{\ell u}(K=1)]^2} \frac{v_{\ell u}(K)}{v_{\ell u}(K=1)} \left\{ \exp \left[\frac{E_u(K) - E_u(K=1)}{kT} \right] \right\} \times \left\{ \exp \left[\frac{h v_{\ell u}(K)}{kT} \right] - 1 \right\} \times \left\{ \exp \left[\frac{h v_{\ell u}(K=1)}{kT} \right] - 1 \right\}^{-1}. \quad (10)$$

The first fraction appearing on the right-hand side of Eq. (10) is given by results obtained by Hill and Van Vleck⁸ as written in convenient form by Earls⁹

⁸ E. Hill and J. H. Van Vleck, Phys. Rev. 32, 250 (1928).

⁹ L. T. Earls, Phys. Rev. 48, 423 (1935).

and tabulated by Dieke and Crosswhite⁵. The quantities $\nu_{\ell_u}(K)$ and $E_u(K)$ have also been tabulated.⁵ Relative intensities of spectral lines belonging to the P_1 - and P_2 - branches, $(0,0)$ - band, $^2\Sigma \rightarrow ^2\Pi$ transitions of OH at 3000°K are given in Table I.

(3) Determine $(P_{\max} X)_K$ from the relation

$$(P_{\max} X)_K = (P_{\max} X)_{K=1} \cdot \frac{S_{\ell_u}(K)}{S_{\ell_u}(K=1)} \cdot \frac{\nu_{\ell_u}(K=1)}{\nu_{\ell_u}(K)} \quad (11)$$

and evaluate

$$\xi'(K) = [1 - \exp -(P_{\max} X)_K]. \quad (12)$$

(4) Calculate

$$(I_{\max})_K = \xi'(K) [R^0(\nu_{\ell_u})]_K. \quad (13)$$

(5) Finally calculate $\log (I_{\max})_K - \log \left\{ S_u(K) [\nu_{\ell_u}(K)]^2 [\nu_{\ell_u}(K)]^3 \right\}$ and plot this quantity as a function of $E_u(K)$. From the slope of this plot determine the apparent population temperature T_u' in the usual way by applying Eq. (7).

The results of calculations carried out according to the scheme outlined above are summarized in Fig. 1 for the P_1 - branch for various assumed values of $\xi'(1)$, in Fig. 2 for the P_1 - and P_2 - branches with $\xi'(1) = 0.90$ for the P_1 - branch, and in Fig. 3 for the P_1 - and P_2 - branches with $\xi'(1) = 0.50$ for the P_1 - branch.

III. DISCUSSION OF RESULTS

Analysis of the data listed in Fig. 1 leads to the conclusions enumerated below.

(1) For sufficiently small values of $\xi'(1)$ the apparent and true values of the population temperatures are identical since Eq. (7) applies in good approximation.

(2) As the value of $\xi'(1)$ is increased, the plots constructed according to Eq. (7) show increasing curvature for the more intense rotational lines until for $\xi'(1) = 0.5$ and greater the constructed curves simulate population temperatures which are of the same order of magnitude as the values reported for flames. It is easy to see how a limited number of experimental points between $K = 3$ and $K = 20$ can be correlated by two intersecting straight lines. We offer this observation as a possible explanation for the reported anomalous values of the population temperatures of OH. Apparent population temperatures T_u' obtained for lines with $10 \leq K \leq 18$ for the P_1 - branch, (0,0)-band, and $2 \Sigma \rightarrow 2 \Pi$ transitions of OH at 3000°K are listed in Table II as a function of the assumed value of $\xi'(1)$.

(3) For sufficiently large values of K , all of the curves become parallel independently of the assumed values of $\xi'(1)$. Thus all of the experimental data yield apparent population temperatures which are in agreement with the true value of the population temperature. Hence, by extending experimental studies to sufficiently large values of K , it is always possible to obtain unambiguous estimates of the true population temperature. Since the slope of plots constructed according to Eq. (7) always approaches, as a lower limit, the slope corresponding to the true population temperature, it is possible that the falling off in intensity for spectral lines with large values of K is not produced by predissociation¹ but is rather the result of falsification of experimental data by self-absorption. This last conclusion is supported also by the data plotted in Figs. 2 and 3 which show that some of the lines belonging to the P_1 - branch fall below the corresponding lines belonging to the P_2 - branch. Gaydon and Wolfhard reported preferential weakening for large values of K for lines belonging to the P_1 - branch for (1,0)- and (2,1)- bands. On the other hand, for the (0,0)- band the small calculated separation seems to increase for lines with larger spectral emissivities (Compare Figs. 2 and 3).

(4) Additional support for our contention that emission spectra may have been

misinterpreted, is obtained by noting that estimates of $\xi'(1)$ for $2\Sigma \rightarrow 2\Pi$ transitions and the (0,0)-band, which are based on the best available absolute intensity measurements for lines of OH,⁷ lead to the conclusion that $\xi'(1)$ is generally so large that extensive self-absorption must occur for representative combustion flames (I). Finally, examination of the data used by Gaydon and Wolfhard¹ to establish predissociation in the (1,0)- and (2,1)-bands shows that the experimental results yield lower values for the population temperature for the weaker spectral lines.

In conclusion it appears appropriate to call attention to the fact that the experimental results of Gaydon and Wolfhard for large values of K and (1,0)- or (2,1)-bands yield rotational temperatures for acetylene-oxygen flames which are clearly lower than the adiabatic flame temperature. These results may indicate simply that the effective temperature in the center of the luminous zone is lower than the equilibrium temperature for complete combustion. The data may also support the predissociation mechanism of Gaydon and Wolfhard.¹ It is evident that a decision between these two alternate interpretations can be reached by careful experimental study of population temperatures in low-pressure flames as a function of position in the flame, using preferentially the experimental results obtained for large values of K. The fact that the observed separation between lines belonging to the P_1 - and P_2 -branches is in agreement with the direction of separation predicted from a study of self-absorption, leads us to the conclusion that the predissociation mechanism requires support by further careful experimental study.

Table I. Relative intensities of spectral lines belonging to the P₁- and P₂- branches, (0,0)- band, and $^2\Sigma \rightarrow ^2\Pi$ transitions of OH, at 3000°K [$S_{P_2(2)}/S_{P_1(1)} = 0.496$]

<u>K</u>	<u>$S_{P_1(K)}/S_{P_1(1)}$</u>	<u>$S_{P_2(K)}/S_{P_2(2)}$</u>
1	1.00	
2	1.29	1.00
3	1.59	1.86
4	1.83	2.61
5	2.00	3.22
6	2.09	3.63
7	2.11	3.84
8	2.05	3.90
9	1.94	3.80
10	1.79	3.58
11	1.61	3.28
12	1.41	2.92
13	1.21	2.53
14	1.02	2.15
15	0.842	1.79
16	0.681	1.46
17	0.541	1.16
18	0.421	0.912
19	0.323	0.702
20	0.244	0.533
21	0.181	0.397
22	0.132	0.291
23	0.0954	0.210
24	0.0678	0.150
25	0.0475	0.105
26	0.0328	0.0730
27	0.0224	0.0500
28	0.0151	0.0338
29	0.0101	0.0226
30	0.0067	0.0149

Table II. Apparent population temperatures T_u' obtained from lines with $10 \leq K \leq 18$ for the F_1 - branch, (0,0)- band, and $2 \Sigma \rightarrow 2 \Pi$ transitions of OH at 3000°K , as a function of assumed values of $\xi' (1)$.

<u>$\xi' (1)$</u>	<u>$T_u', ^\circ\text{K}$</u>
0.1	3,000
0.3	3,000
0.5	~ 3,500
0.7	~ 5,000
0.9	~ 6,500
0.95	~ 10,000
0.999	~ 19,000

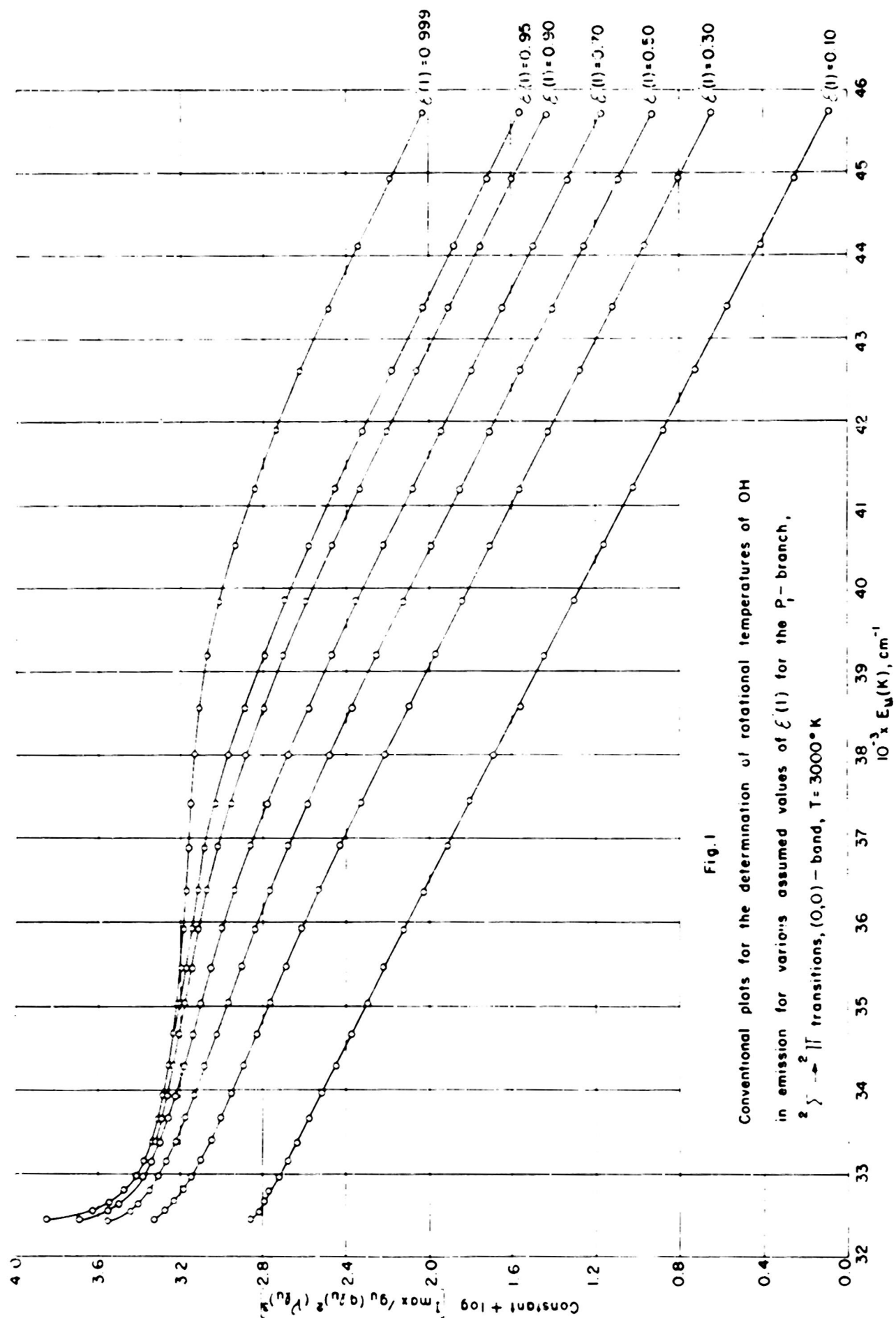


Fig. 1
Conventional plots for the determination of rotational temperatures of OH
in emission for various assumed values of $\xi(l)$ for the P_1 -branch,
 $2\Sigma \rightarrow 2\Pi$ transitions, (0,0) - band, $T = 3000^\circ\text{K}$

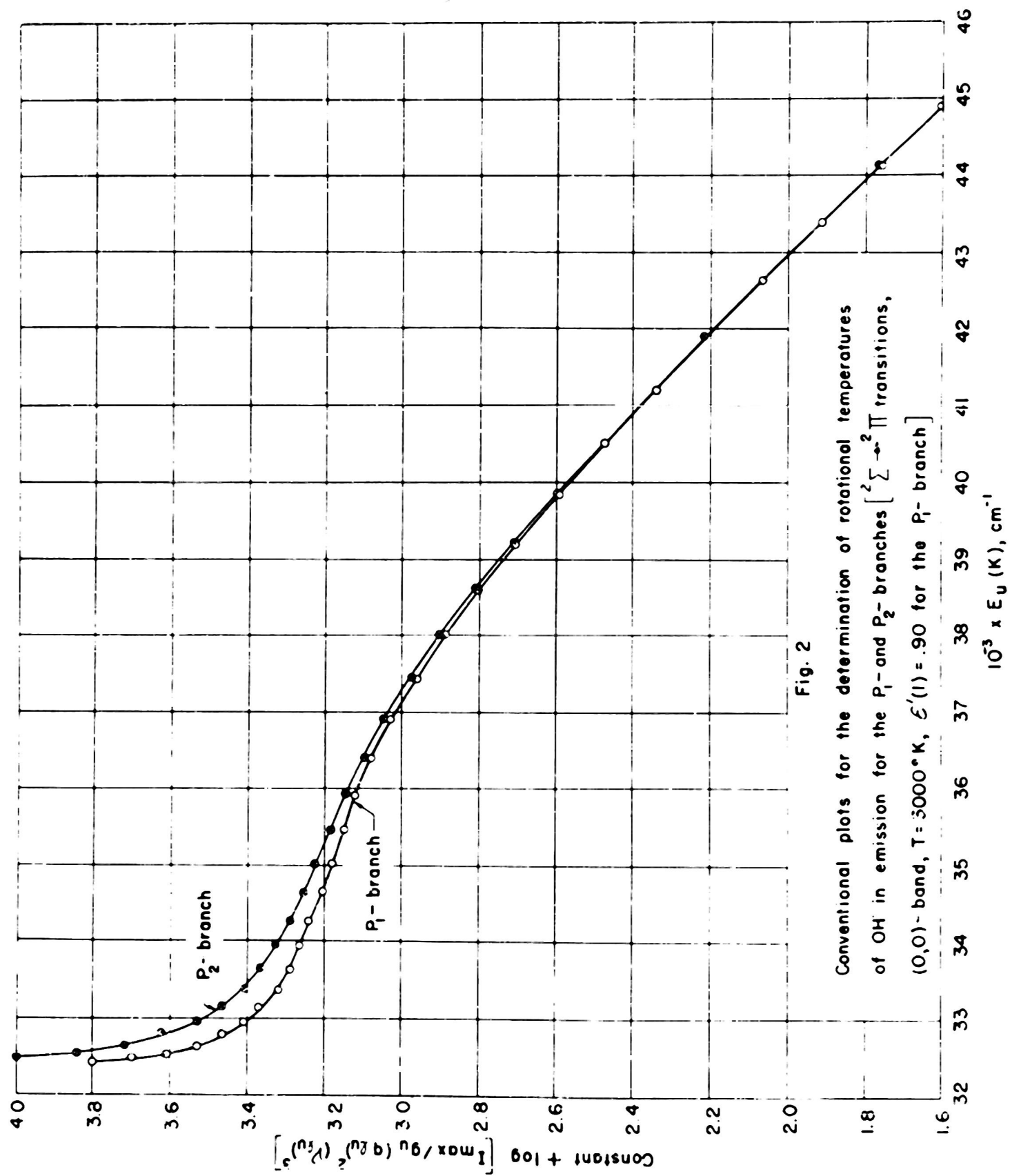


Fig. 2
Conventional plots for the determination of rotational temperatures
of OH in emission for the P_1 - and P_2 -branches $[\sum \sum \Pi \text{ transitions,}$
 $(0,0)$ -band, $T = 3000^\circ\text{K}$, $\mathcal{E}'(1) = .90$ for the P_1 -branch]

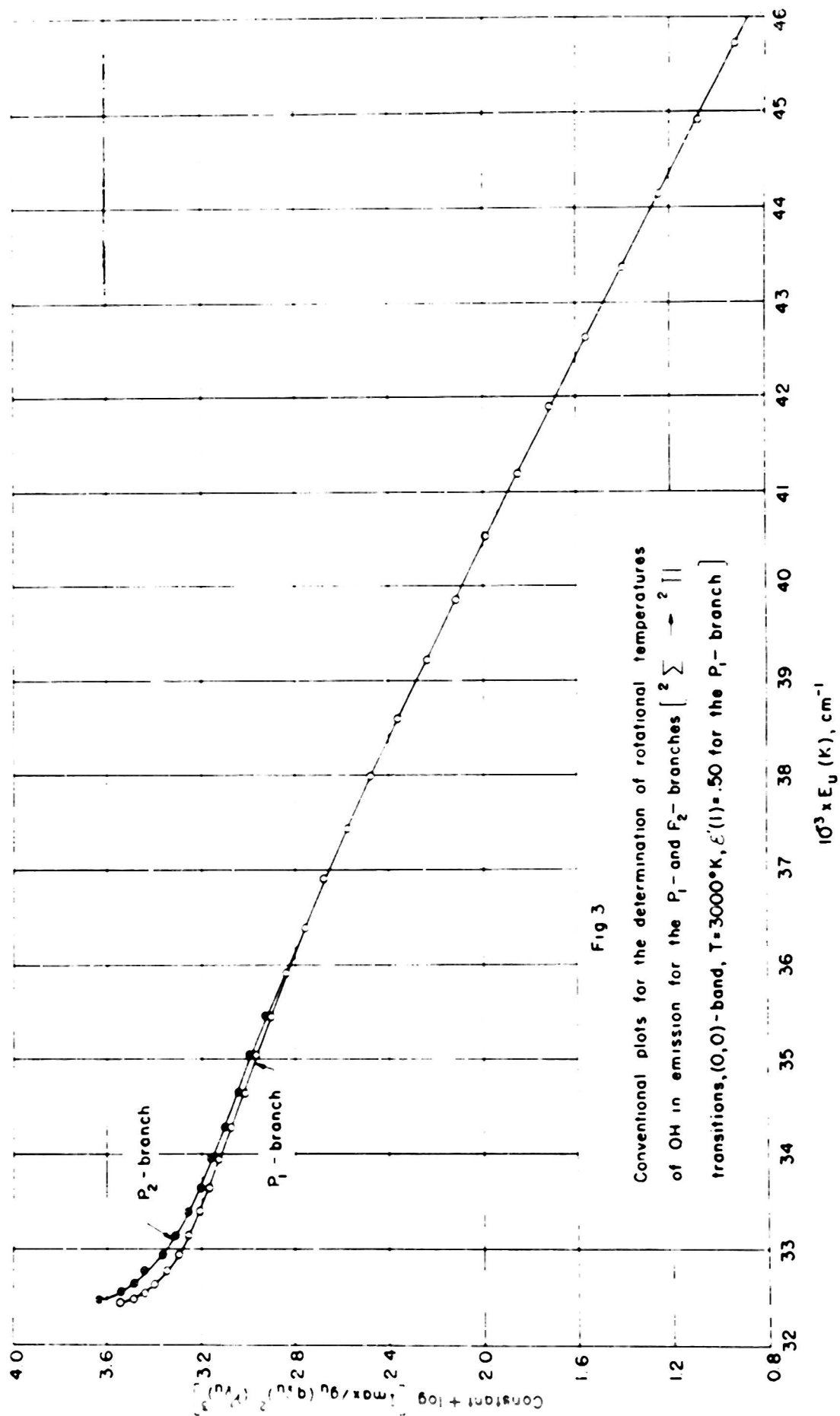


Fig 3

Conventional plots for the determination of rotational temperatures of OH in emission for the P₁- and P₂-branches [$\sum \frac{2}{J+1}$] transitions, (0,0)-band, T=3000°K, $\epsilon'(1)=.50$ for the P₁-branch]

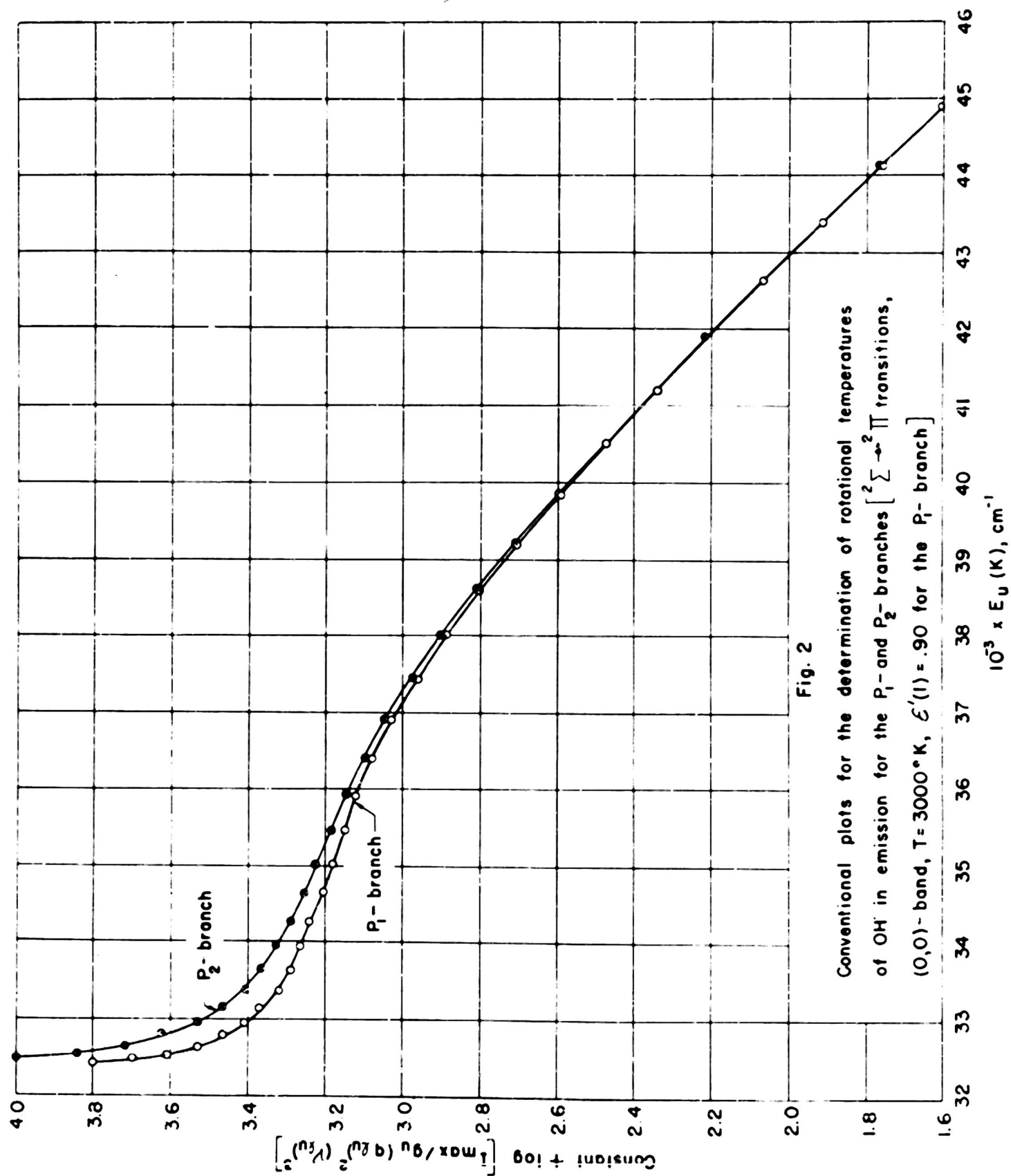


Fig. 2
Conventional plots for the determination of rotational temperatures
of OH in emission for the P_1 - and P_2 -branches [$^2\Sigma \rightarrow ^2\Pi$ transitions,
(0,0)-band, $T = 3000^\circ\text{K}$, $\mathcal{E}'(1) = .90$ for the P_1 -branch]

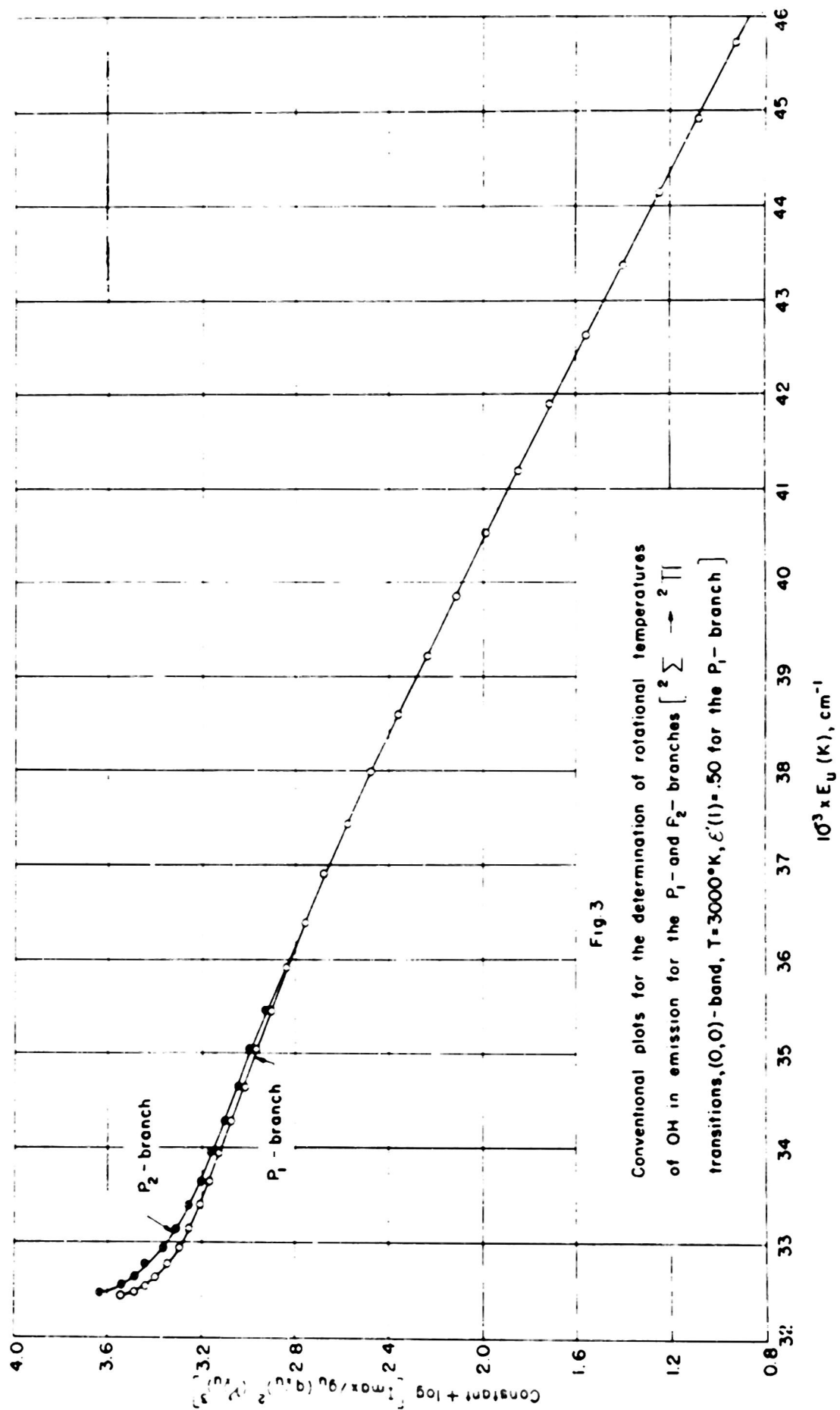


Fig 3

Conventional plots for the determination of rotational temperatures of OH in emission for the P_1 - and P_2 -branches [$\sum_{l=0}^{\infty} (2l+1) \exp(-E_l/kT)$] transitions, (0,0)-band, $T=3000^\circ\text{K}$, $E'(l)=.50$ for the P_1 -branch]

APPENDIX I. BASIC RELATIONS IN TERMS OF TOTAL EMITTED INTENSITIES

The expressions given in Eqs. (7) and (8) require slight modifications when total intensity ratios rather than peak intensity ratios are available. If the apparent integrated intensity of the spectral line with center at the frequency $\nu_{\ell u}$ is denoted by the symbol $A(\nu_{\ell u})$, then, as is well-known,¹⁰

$$A(\nu_{\ell u}) \approx R^0(\nu_{\ell u}) (mc^2 / 2\pi kT_t \nu_{\ell u}^2)^{-\frac{1}{2}} (P_{\max} X) \left\{ \sum_{n=0}^{\infty} \left[(n+1)^{\frac{1}{2}} (n+1)! \right]^{-1} (-P_{\max} X)^n \right\}. \quad (A-1)$$

From Eqs. (1) and (A-1) it follows that

$$I_{\max} = \left[A(\nu_{\ell u}) / \nu_{\ell u} \right] (mc^2 / 2\pi kT_t)^{\frac{1}{2}} \mathcal{Z} \quad (A-2)$$

where

$$\mathcal{Z} = \left\{ (P_{\max} X) \sum_{n=0}^{\infty} \left[(n+1)^{\frac{1}{2}} (n+1)! \right]^{-1} (-P_{\max} X)^n \right\}^{-1} [1 - \exp(-P_{\max} X)]. \quad (A-3)$$

Since $\mathcal{Z} = 1$ for $P_{\max} X \ll 1$, it is apparent from Eqs. (7) and (A-2) that

$$\frac{\partial \ln \left[A(\nu_{\ell u}) / \nu_{\ell u}^4 \varepsilon_u(q_{\ell u})^2 \right]}{\partial T_u} = - \frac{1}{kT_u} \quad \text{for } \xi' \ll 1 \text{ for all lines.} \quad (A-4)$$

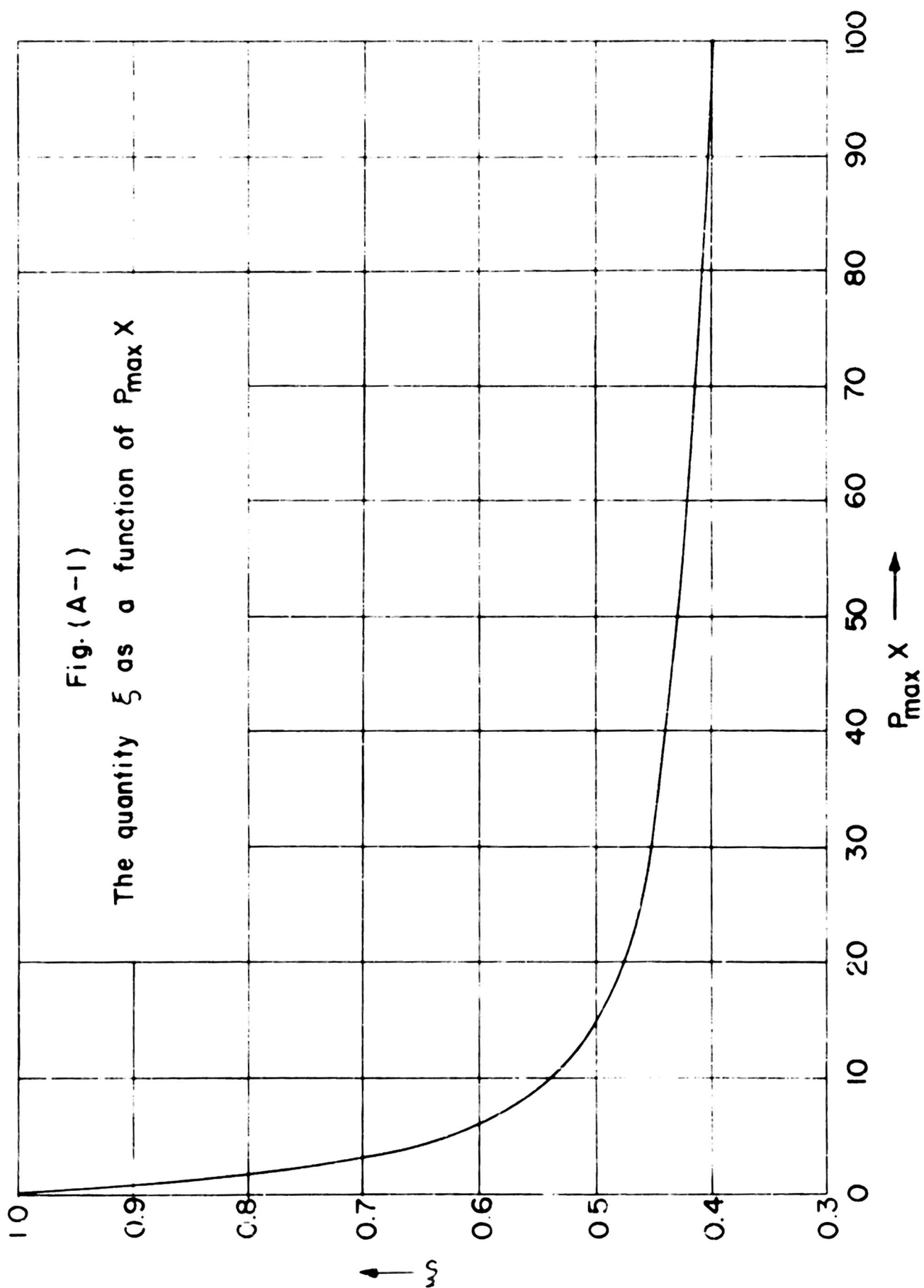
Equation (A-4) is the expression which is usually employed for the interpretation of experimental data. The value of \mathcal{Z} is plotted as a function of $P_{\max} X$ in Fig. (A-1).

When conventional plots for the determination of population temperatures are constructed according to Eq. (A-4) for arbitrary values of $\xi' (1)$, results substantially equivalent to those shown in Fig. 1 are obtained. In this case the quantity $A(\nu_{\ell u})$ can be calculated from Eq. (A-2) after obtaining I_{\max} by use of the procedure described in Section IIB. Construction of curves analogous

¹⁰ R. Ladenburg, Zeits. f. Physik 65, 200 (1930).

to those shown for the P_1 - and P_2 - branches in Figs. 2 and 3 leads to the conclusion that the separation between lines belonging to the P_1 - and P_2 - branches is slightly decreased. Thus, although the direction of separation between lines belonging to the P_1 - and P_2 - branches is the same as observed by Gaydon and Wolfhard,¹ there is a discrepancy between the quantitative behavior of intensity as a function $E_{\mu}(K)$ for large values of K . In this connection it may be of interest to note that the splitting between branches for large values of K has not been observed for the (0,0)- band by Gaydon and Wolfhard.

Fig. (A-1)
The quantity ξ as a function of $P_{\max} X$



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Representative absorption studies for the determination of rotational temperatures in flames have been analyzed for the P_1 -branch, (0,0)-band, $2\pi \rightarrow 2\Sigma$ transitions of OH at 3000°K. The calculations show that erroneous interpretation of experimental results occurs if the product of maximum absorption coefficient (P_{\max}) and optical density (X) is not small compared to unity. Sample calculations for a blackbody light source show that the customary procedure for treating experimental results will permit adequate correlation of the data by straight lines up to relatively large values of $P_{\max} X$. It is remarkable that the preceding statement remains true even under conditions in which emission data for the $2\Sigma \rightarrow 2\pi$ transitions clearly indicate that $P_{\max} X$ is no longer small compared to unity. The apparent rotational temperature of the ground electronic state varies by only a few hundred degrees when the temperature of the light source is increased from 3500°K to 8000°K, the direction of the change being such that the apparent temperatures of the flame are the more nearly in agreement with the actual temperature of the flame the higher the temperature of the light source. The calculations emphasize the fact that correlation of experimental data by straight lines is no assurance that an error in interpretation is not being made. We believe that the data presented in this article cast doubt upon the significance of absolute values of rotational temperatures obtained from conventional interpretation of experimental data on absorption by OH in flames.

I. INTRODUCTION

The experimental data and the effect of self-absorption on population temperatures in emission experiments have been reviewed in the preceding article.¹ It is the purpose of the present analysis to indicate briefly possible effects of large values² of $P_{\max} X$ on apparent population temperatures T_2 obtained in absorption experiments for spectral lines with Doppler contour. The results of calculations for $2\pi \rightarrow 2\Sigma$ transitions of OH and the (0,0)-band show that the apparent population temperature is strongly dependent on the absolute numerical value of $P_{\max} X$ and relatively insensitive to the temperature of the light source, as long as the source is appreciably hotter than the flame. Hence it must be concluded that the available experimental data on absorption experiments for the determination of the population temperature of the ground state cannot be interpreted unequivocally to represent the actual population temperature of the ground state.

* Supported by the O.N.R. under contract Nonr-220(03), NR 015 210.

[†] Numerical calculations were performed by Mrs. B. MacDonald.

¹ S. S. Penner, J. Chem. Phys. (in press). Hereafter referred to as II.

² For estimates of the magnitude of $P_{\max} X$ in low-pressure flames see S. S. Penner, J. Chem. Phys. (in press). Hereafter referred to as I.

II. THE EFFECT OF SELF-ABSORPTION ON APPARENT POPULATION TEMPERATURES IN ABSORPTION EXPERIMENT

At thermodynamic equilibrium the spectral emissivities and absorptivities arising from a given transition are identical. Hence it is to be expected that falsification of experimental data in absorption experiments needs to be considered whenever self-absorption is known to be of importance in emission. The following analysis is restricted to the use of peak intensities for the calculation of population temperatures.*† Instrumental distortion will be neglected as in II.

A. Equations for the Determination of Apparent Population Temperatures

In an absorption experiment with a source which is much brighter than the emission lines and which emits the spectral radiant intensity $R_S(\nu)$,* the maximum value of the fractional absorbed intensity, $\alpha' = A_{\max}/R_S(\nu_{\ell u})$, is given by the expression

$$\alpha' = 1 - \exp(-P_{\max} X) \quad (1)$$

whence, proceeding as for emission (II),

$$-\alpha' = \sum_{n=1}^{\infty} x^n/n!$$

and

$$-x = \alpha' \left[1 + \frac{1}{2} \alpha' + (1/3)(\alpha')^2 + (1/4)(\alpha')^3 + \dots \right]. \quad (2)$$

For $\alpha' \ll 1$, Eq. (2) reduces to the expression $-x = \alpha'$ or

$$(S_{\ell u} X) (mc^2/2\pi k T_t \nu_{\ell u}^2)^{\frac{1}{2}} = A_{\max}/R_S(\nu_{\ell u}) \quad (3)$$

where (I)

$$S_{\ell u} X \simeq (8\pi^3 N/3hc^2) \nu_{\ell u}^2 \epsilon_{\ell u} q_{\ell u}^2 [\exp(-E_{\ell}/k T_t)]. \quad (4)$$

* For definitions and symbols which correspond to those used in the study of emission experiments see II, or I.

† The use of apparent total absorption measurements is discussed briefly in the Appendix.

Here T_l is the population temperature of the ground (initial) state in an absorption experiment. From Eqs. (3) and (4) it is readily shown (1) that for greybody emitters, with the effective temperature of the source, T_s , large compared to T_l ,

$$\frac{\partial \ln [A_{\max}/\epsilon_u q_{lu}^2]}{\partial E_l} = -\frac{1}{kT_l} \quad (5)$$

For arbitrary values of α' , Eq. (5) should be replaced by the expression

$$\frac{\partial \ln \left\{ A_{\max} \left[1 + \frac{1}{2} \alpha' + (1/3) (\alpha')^2 + (1/4) (\alpha')^3 + \dots \right] / \epsilon_u (q_{lu})^2 \right\}}{\partial E_l} = -\frac{1}{kT_l} \quad (6)$$

From Eq. (6) it is evident that T_l can, in general, be determined only if absolute values of α' are known.

B. A Method for Demonstrating the Effect of Self-Absorption on Apparent Population Temperatures of OH ($2\Pi \rightarrow 2\Sigma$ Transitions)

We proceed to examine quantitatively the effect of absolute values of α' on apparent population temperatures determined according to Eq. (5). Plots of $\log [A_{\max}/\epsilon_u (q_{lu})^2]$ as a function of E_l can be constructed by using the following scheme.

(1) Assume a value of α' , for example, for the P_1 - branch, (0,0)- band, for the transition identified by the index $K = 1$, using the notation of Dieke and Crosswhite.³ Next calculate $\alpha'(K)$ by using the same procedure as was used to obtain the maximum values of the spectral emissivity for the line with index K (II).

(2) Calculate

$$A_{\max} = \alpha'(K) B_g (q_{lu}) \quad (7)$$

³ G. H. Dieke and H. M. Crosswhite, The Ultraviolet Bands of OH. The Johns Hopkins University, Bumblebee Series Report No. 87, 1948.

assuming a blackbody distribution curve for the source at the temperature T_s .

(3) Calculate $\log \left\{ (A_{\max})_K / \epsilon_u(K) [q_{\lambda}(K)]^2 \right\}$ and plot this quantity as a function of $E_{\ell}(K)$. From the slope of this plot determine the apparent population temperature T_{ℓ}' in the usual way by applying Eq. (5).

The results of calculations carried out according to the scheme outlined above are summarized in Figs. 1 to 4 for α' ($K=1$) of P_1 - branch = 0.1, 0.3, 0.7, and 0.9, respectively, for two or more values of the source temperature T_s . Apparent population temperatures for the relevant experimental conditions are indicated in Figs. 1 to 4.

III. DISCUSSION OF RESULTS

Analysis of the data presented in Figs. 1 to 4 leads to the conclusions enumerated below.

(1) Experimental data treated according to conventional procedures permits correlation of results by linear plots even for values of α' ($K=1$) of the P_1 - branch which are so large that T_{ℓ}' differs appreciably from T_{ℓ} . Hence absolute values obtained for T_{ℓ}' cannot be considered to be meaningful without convincing proof that $P_{\max}X$ is sufficiently small for the spectral lines under study to justify conventional treatment of data.

(2) Apparent population temperatures T_{ℓ}' are always larger than T_{ℓ} . The difference between T_{ℓ}' and T_{ℓ} decreases somewhat as the temperature of the light source is increased, for fixed values of $P_{\max}X$. However, the apparent temperatures are relatively insensitive to the numerical value of T_s , decreasing by only a few hundred degrees as T_s is raised from 3500°K to 8000°K.

(3) For sufficiently large values of α' ($K=1$) for the P_1 - branch, discontinuities or curvatures are observed in the conventional plots which are reminiscent of the results obtained in emission experiments (II).

(4) Comparison with estimates of $\alpha'(K=1)$ based on the absolute intensity measurements performed by Oldenberg and his collaborators,⁴ shows that

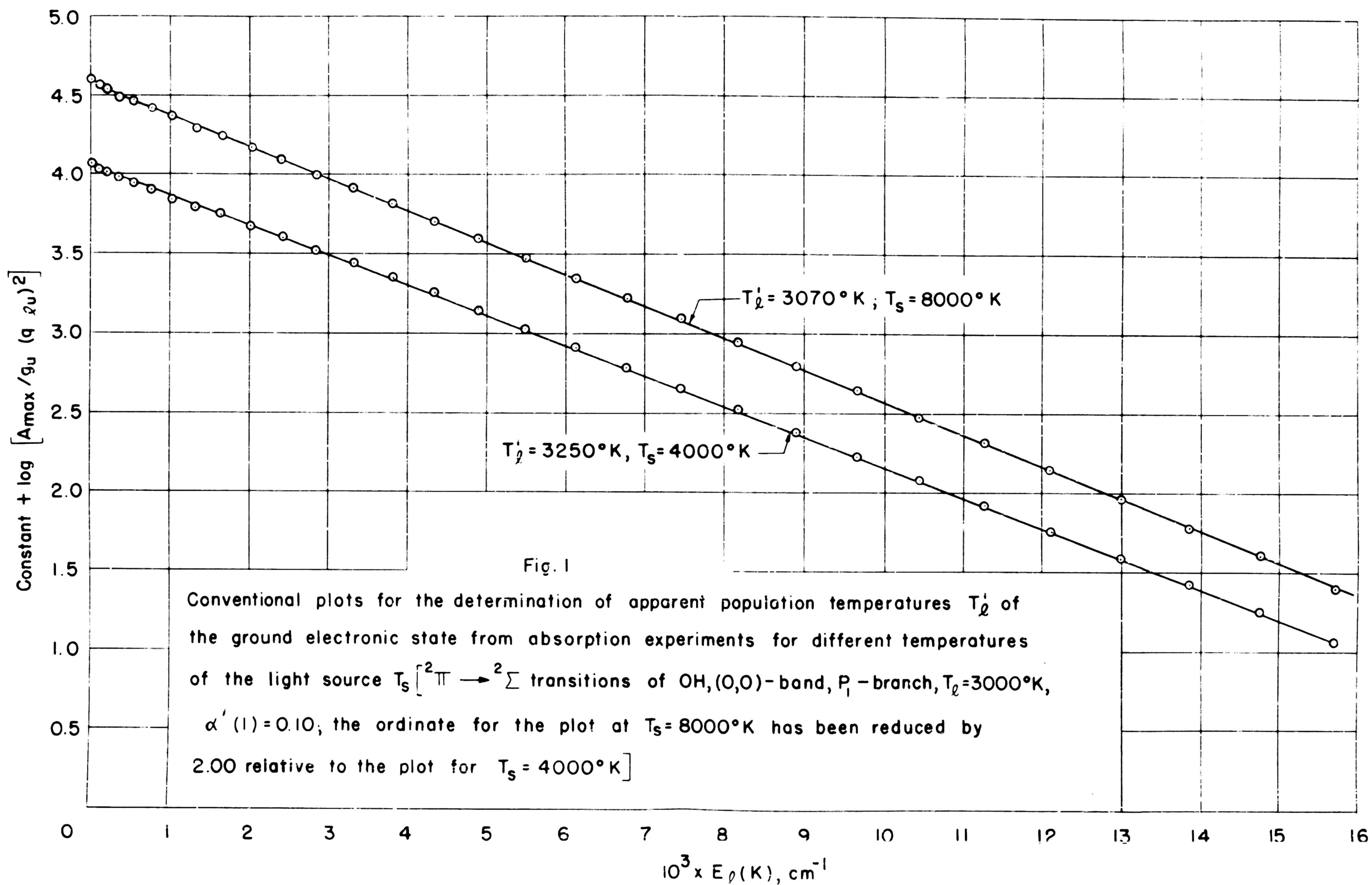
$\alpha'(K=1)$ for the P_1 -branch is too large to permit the determination of rotational temperature by the use of Eq. (5) unless care is taken to utilize only spectral lines with large values of K . The particular values of K which can be used depend evidently on the absolute value of $\alpha'(K=1)$.

Adequate care in the interpretation of absorption studies, as well as of emission studies, permits the determination of both the true rotational temperature and of the concentration of the absorbing or emitting species, provided the population of molecules in the rotational energy levels obeys the Maxwell-Boltzmann distribution law. Thus data on spectral lines with large K can be used to obtain T_L . Next a family of curves, for the known values of T_L and T_S , is constructed, for example, for different values of $\alpha'(K=1)$ for the P_1 -branch (compare Figs. 1 to 4). The data obtained by using Eq. (5) for the lower values of K can then be employed to determine $\alpha'(K=1)$ whence the optical density X is determined since S_{L_u} is known.⁴

In conclusion it appears desirable to call attention to the fact that some of the published experimental measurements on absorption by OH in flames suggest the same sort of curvatures as would be obtained if a curve were drawn through the calculated data shown in Figs. 1 to 4.⁵

⁴ R. J. Dwyer and O. Oldenberg, J. Chem. Phys. 12, 351 (1944); O. Oldenberg and F. F. Pieke, J. Chem. Phys. 6, 439 (1938).

⁵ H. P. Broida, J. Chem. Phys. 19, 1383 (1951), Cf. Fig. 5.



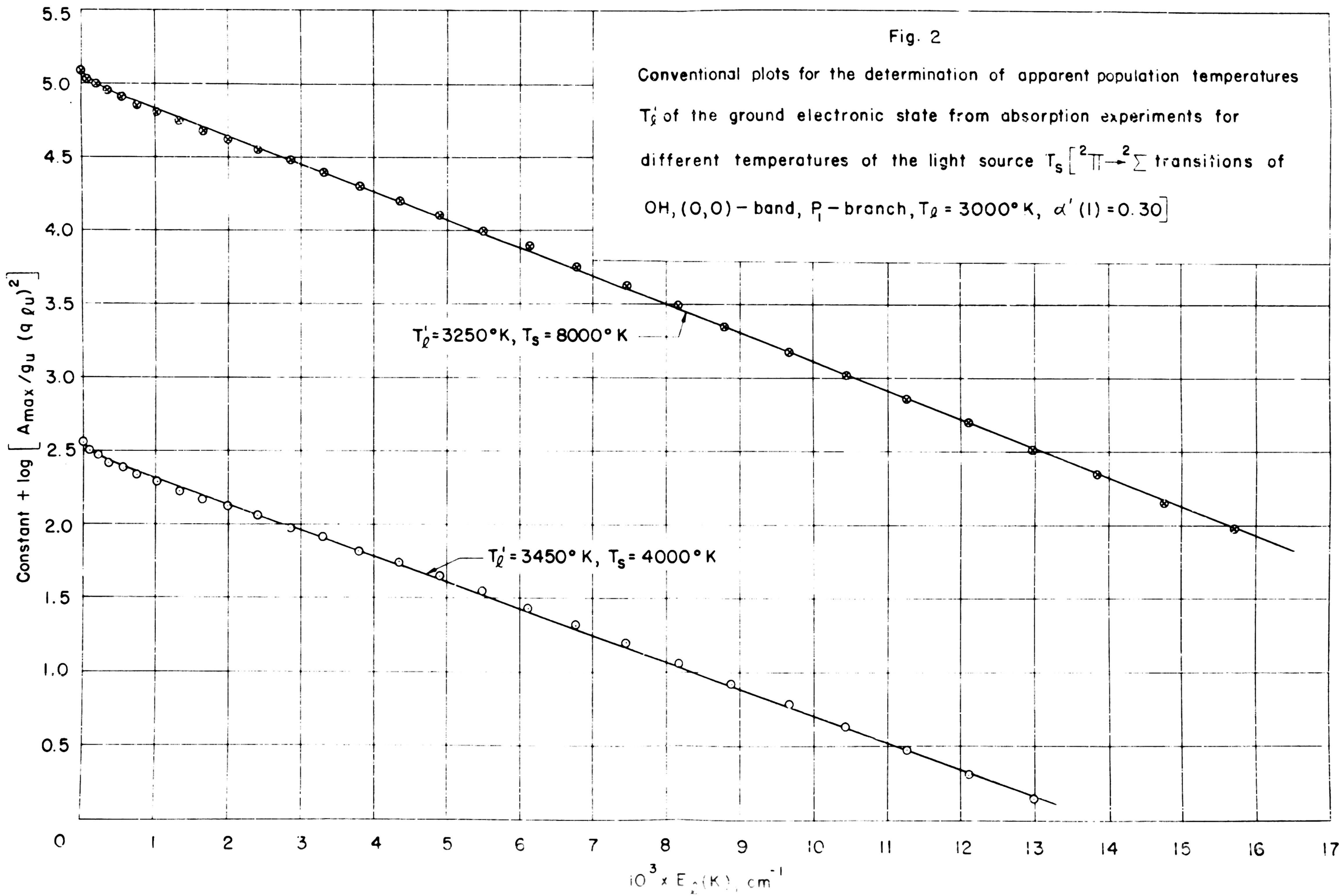


Fig. 2

Conventional plots for the determination of apparent population temperatures T'_l of the ground electronic state from absorption experiments for different temperatures of the light source T_s [$^2\Pi \rightarrow ^2\Sigma$ transitions of OH, (0,0) - band, P_1 - branch, $T_l = 3000^\circ\text{K}$, $\alpha'(1) = 0.30$]

$T'_l = 3250^\circ\text{K}$, $T_s = 8000^\circ\text{K}$

$T'_l = 3450^\circ\text{K}$, $T_s = 4000^\circ\text{K}$

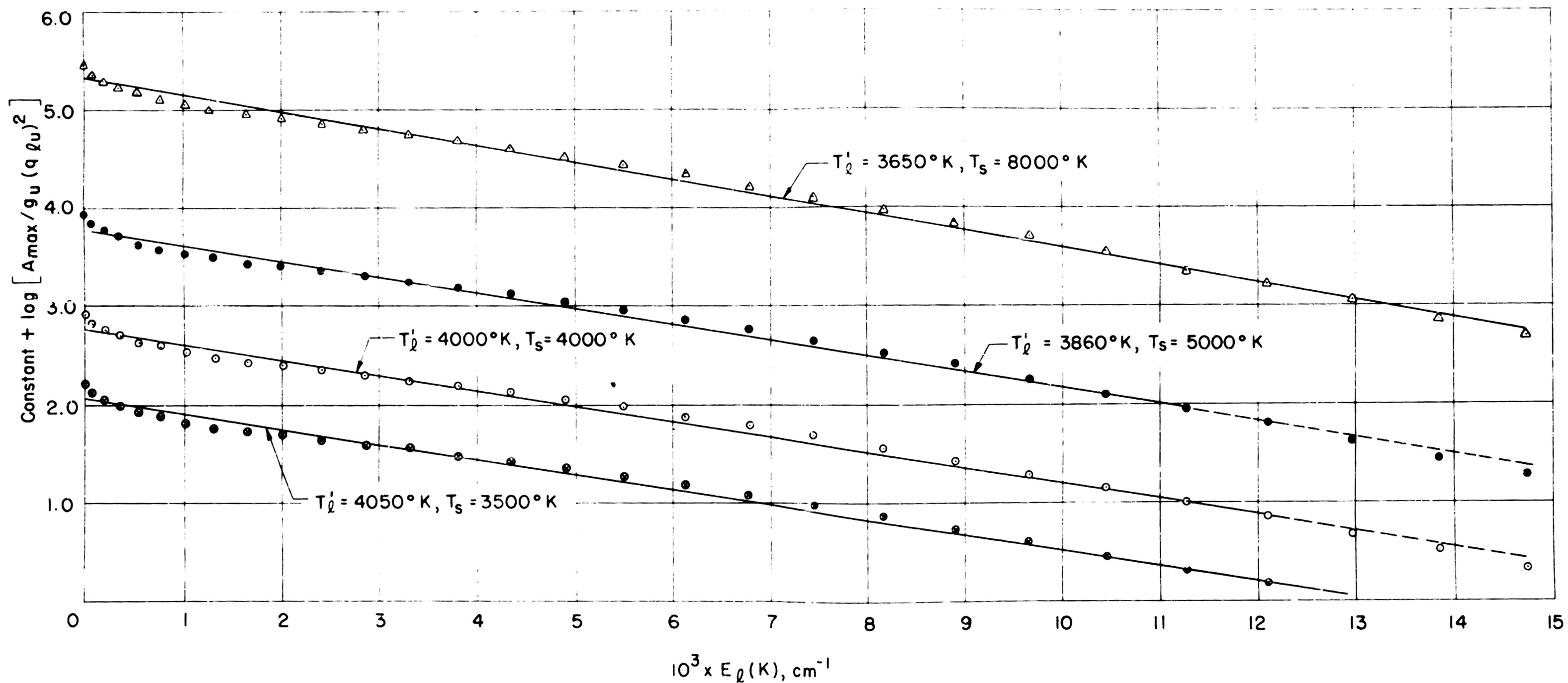
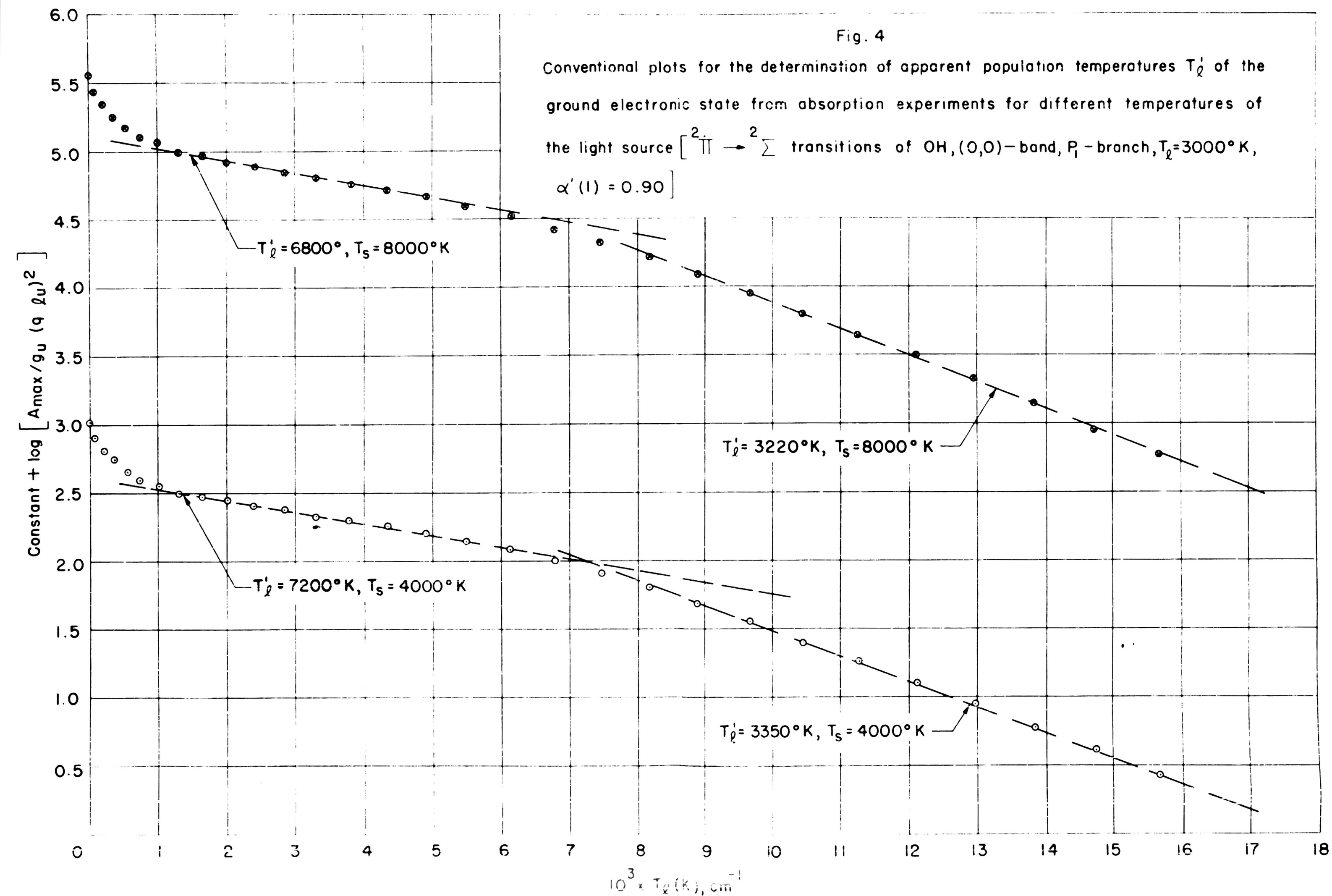


Fig. 3

Conventional plots for the determination of apparent population temperatures T'_l of the ground electronic state from absorption experiments for different temperatures of the light source $[^2\Pi \rightarrow ^2\Sigma]$ transitions of OH, (0,0)-band, P_1 -branch, $T_l = 3000^\circ\text{K}$, $\alpha(1) = 0.70$

Fig. 4

Conventional plots for the determination of apparent population temperatures T'_ℓ of the ground electronic state from absorption experiments for different temperatures of the light source [$^2\Pi \rightarrow ^2\Sigma$ transitions of OH, (0,0)-band, P_1 -branch, $T_\ell = 3000^\circ\text{K}$, $\alpha'(1) = 0.90$]



APPENDIX. POPULATION TEMPERATURES BASED ON APPARENT TOTAL ABSORPTION MEASUREMENTS FOR SPECTRAL LINES WITH DOPPLER CONTOUR

It is readily shown that the apparent total absorption A_T is related to the peak absorption A_{max} through the expression

$$A_{max} = A_T \cdot \zeta \cdot (V_{\ell u})^{-1} (mc^2/2\pi kT_t)^{\frac{1}{2}} \quad (A-1)$$

where¹

$$\zeta = [1 - \exp(-P_{max} X)] (P_{max} X)^{-1} \left\{ \sum_{n=0}^{\infty} [(n+1)^{\frac{1}{2}} (n+1)!]^{-1} (P_{max} X)^n \right\}^{-1} \quad (A-2)$$

By the use of Eqs. (A-1) and (A-2) it is a simple matter to convert the data given in Figs. 1 to 4 to the corresponding plots involving A_T . The values of ζ as a function of $P_{max} X$ have been given in Fig. (A-1) of II. Conclusions derived from conventional plots in terms of A_T for estimating population temperatures do not differ significantly from the material given in Section III, for the range of spectral emissivities considered in the present analysis.

Apparent Population Temperatures for OH in Flames. IV. Isointensity
Method for Emission Experiments*

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Representative calculations to determine observable peak and total intensity ratios in emission for spectral lines with Doppler contour have been carried out for $2 \Sigma \rightarrow 2 \Pi$ transitions, (0,0)- band, P₁- branch of OH at 3000°K. The calculations show that the ratios of peak and total intensities are functions of absolute values of the products of maximum absorption coefficients (P_{\max}) and optical density (I) for the lines under study. Hence quantitative interpretation of experimental data is not possible unless proper account is taken of the influence of absolute intensities on experimental results.

I. INTRODUCTION

In earlier publications of this series we have examined the basic relations,¹ the conventional procedure for the determination of population temperatures from emission studies,² and the conventional procedure for the determination of population temperature from absorption experiments.³ These investigations have shown that a simple explanation for apparent flame temperature anomalies can be obtained by taking proper account of the effect of absolute values of maximum spectral emissivities on experimental results. It is the purpose of the present analysis to investigate the influence of absolute values of spectral emissivities on the use of the isointensity method.^{4,5} Representative calculations have been

* Supported by the O.N.R. under contract Nonr-220(03), NR 015 210.

¹ S. S. Penner, J. Chem. Phys. (in press). Hereafter referred to as I.

² Part II.

³ Part III.

⁴ G. H. Dieke and H. M. Crosswhite, The Ultraviolet Bands of OH,
The Johns Hopkins University, Bumblebee Series Report No. 87, 1948.

⁵ K.E. Shuler, J. Chem. Phys. 18, 1466 (1950).

carried out for $^2\Sigma \rightarrow ^2\Pi$ transitions of OH at 3000°K for the (0,0)- band and the P_1 - branch. The results of the present analysis show that reported flame temperature anomalies, obtained by use of the isointensity method, may be the result of failure to allow for the effect of absolute values of the spectral emissivity on the peak and total intensities of spectral lines with Doppler contour.*

II. OUTLINE OF CALCULATIONS

Two spectral lines, which are differentiated by the indices K and K' , appear to have equal peak intensities I_{\max} in an emission experiment if

$$I_{\max}(K) = I_{\max}(K'), \quad (1)$$

where I_{\max} is given by Eq. (1) of II. For various assumed values of ξ' ($K=1$) of the P_1 - branch at 3000°K , it is a simple matter to calculate the ratios $I_{\max}(K)/I_{\max}(K=1)$ by following the procedure described in II. The results of these calculations are summarized in Table I and representative values are plotted in Fig. 1.*

The spectral lines, which are identified by the indices K and K' , appear to have equal total intensities in emission if

$$A(K) = A(K') \quad (2)$$

where

$$A(K) = \left[R^0_{\nu_{\ell u}} (mc^2/2\pi kT_t)^{-\frac{1}{2}} \nu_{\ell u}(K) \right] \left[P_{\max}(K)X \right] \sum_{n=0}^{\infty} \left[(n+1)^{\frac{1}{2}}(n+1)! \right]^{-1} \left[-P_{\max}(K)X \right]^n. \quad (3)$$

By proceeding according to the method described in the Appendix of II, it is readily shown that

$$A(K)/A(K') = \left[I_{\max}(K')/I_{\max}(K) \right] \left[\nu_{\ell u}(K)/\nu_{\ell u}(K') \right] \left[\zeta(K')/\zeta(K) \right]. \quad (4)$$

Representative numerical values of $A(K)/A(K')$ are listed in Table II and plotted

* For definitions and symbols see the previous papers of this series.

in Fig. 2 for $^2 \Sigma \rightarrow ^2 \Pi$ transitions of OH at 3000°K for the (0,0)- band and the P_1 - branch.

III. DISCUSSION OF RESULTS

Reference to the data listed in Tables I and II and plotted in Figs. 1 and 2 shows that the ratios $I_{\max}(K)/I_{\max}(K')$ and $A(K)/A(K')$ are functions of the value of $\xi'(K=1)$ for the P_1 - branch, the dependence on $\xi'(K=1)$ becoming stronger as $\xi'(K=1)$ approaches unity, i.e., as the extent of self-absorption increases. This observation is emphasized by noting, for example, that the line having absolute peak intensity closest to the line with $K = 3$, has $K = 13$ for $\xi'(1) = 0.1$, $K = 13$ for $\xi'(1) = 0.3$, $K = 14$ for $\xi'(1) = 0.5$, $K = 15$ for $\xi'(1) = 0.7$, $K = 18$ for $\xi'(1) = 0.9$, $K = 19$ for $\xi'(1) = 0.95$, and $K = 21$ for $\xi'(1) = 0.99$. Comparison of the data given in Tables I and II and plotted in Figs. 1 and 2, respectively, also shows that the effect of self-absorption in falsifying the data obtained by use of the iso-intensity method is more pronounced for peak emitted intensities than for total intensities.

It is somewhat difficult to draw general conclusions regarding the effect of self-absorption on reported flame temperatures using the iso-intensity method. However, it is clear that anomalies obtained without regard for the effect of absolute spectral emissivities require reexamination.

The effect of self-absorption on population temperatures determined from the iso-intensity method can be demonstrated graphically by using the procedure developed by Shuler⁵ whose method is equivalent to the assumption that total intensity ratios $A(K)/A(K')$ can be replaced by the product of transition probability ratios $\epsilon_u(K) [q_{lu}(K)]^2 / \epsilon_u(K') [q_{lu}(K')]^2$ and appropriate exponential factors for spectral lines which are close together. Plots of $E(K) - E(K')$ vs. $\log \left\{ \epsilon_u(K) [q_{lu}(K)]^2 / \epsilon_u(K') [q_{lu}(K')]^2 \right\}$ are shown in Fig. 3

as a function of $\xi' (1)$ for pairs of spectral lines for which $I_{\max}(K)/I_{\max}(K')$ is nearly equal to unity. Similarly, plots of $E(K)-E(K')$ vs. $\log \left\{ \epsilon_u(K) [\varphi_{lu}(K)]^2 / \epsilon_u(K') [\varphi_{lu}(K')]^2 \right\}$ are shown in Fig. 4 as a function of $\xi' (1)$ for pairs of spectral lines for which $A(K)/A(K')$ is nearly equal to unity.

Reference to Figs. 3 and 4 shows that the plots deviate progressively more from straight lines as $\xi' (1)$ is increased. Apparent population temperature T_n' are noted on the curves given in Figs. 3 and 4. The results are seen to be an immediate consequence of the dependence of the K - values for lines with equal peak or total intensities on $\xi' (1)$. Hence the conclusion is reached that the effects of self-absorption in distorting experimental data do not necessarily cancel in first order for the isointensity method, although the distortion of data is less marked than for the procedures considered in II and III. A simple physical explanation for failure of the isointensity method at large values of the spectral emissivity is obtained by noting that the quantities $R^0(\nu_{lu})$ influence the observable intensities and that $R^0(\nu_{lu})$, which is a function of temperature, is not the same for any distinguishable pair of spectral lines. Furthermore, equally intense spectral lines, for which $S_{lu}(K) = S_{lu}(K')$, have slightly different widths since the Doppler width is proportional to the frequency of the line center. Thus the conclusion is reached that the effects of self-absorption will cancel exactly only for equally intense spectral lines with line centers occurring at identical frequencies.

Table I. Numerical values of $S_{\mu}(K)/S_{\mu}(1)$ and of $I_{\max}(K)/I_{\max}(1)$ as a function of $\epsilon'(K=1)$ for the P_1 -branch, (0,0)-band, $\sum \rightarrow 2\Pi$ transitions of OH at 3000°K.

K	$S_{\mu}(K)/S_{\mu}(1)$	$I_{\max}(K)/I_{\max}(1)$ for							
		$\epsilon'(1)=0.1$	$\epsilon'(1)=0.3$	$\epsilon'(1)=0.5$	$\epsilon'(1)=0.7$	$\epsilon'(1)=0.9$	$\epsilon'(1)=0.95$	$\epsilon'(1)=0.99$	
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	1.29	1.30	1.26	1.21	1.15	1.08	1.05	1.03	1.03
3	1.59	1.60	1.50	1.39	1.27	1.13	1.08	1.05	1.05
4	1.83	1.86	1.70	1.53	1.35	1.16	1.11	1.07	1.07
5	2.00	2.05	1.85	1.63	1.41	1.19	1.14	1.09	1.09
6	2.09	2.18	1.95	1.70	1.45	1.22	1.16	1.11	1.11
7	2.11*	2.25*	2.00	1.74	1.49	1.25	1.19	1.14	1.14
8	2.05	2.25*	2.02*	1.77*	1.52	1.27	1.22	1.17	1.17
9	1.94	2.20	1.99	1.77*	1.53	1.30	1.24	1.19	1.19
10	1.79	2.09	1.93	1.74	1.54*	1.33	1.27	1.22	1.22
11	1.61	1.94	1.84	1.69	1.53	1.35	1.30	1.26	1.26
12	1.41	1.77	1.72	1.62	1.51	1.37	1.33	1.29	1.29
13	1.21	1.58	1.57	1.52	1.46	1.38*	1.35	1.32	1.32
14	1.02	1.38	1.41	1.40	1.39	1.37	1.37*	1.36	1.36
15	0.842	1.19	1.24	1.26	1.29	1.34	1.36	1.38	1.38
16	0.681	1.00	1.06	1.11	1.17	1.28	1.33	1.40*	1.40*
17	0.541	0.824	0.896	0.956	1.04	1.20	1.27	1.39	1.39
18	0.421	0.564	0.740	0.804	0.899	1.08	1.18	1.34	1.34
19	0.323	0.534	0.600	0.662	0.757	0.954	1.06	1.26	1.26
20	0.244	0.419	0.477	0.533	0.621	0.812	0.926	1.15	1.15
21	0.181	0.323	0.373	0.421	0.498	0.672	0.780	1.00	1.00
22	0.132	0.246	0.286	0.326	0.391	0.540	0.637	0.847	0.847
23	0.0954	0.185	0.217	0.249	0.301	0.424	0.506	0.690	0.690

* An asterisk is used to identify maximum intensity ratios.

Table I. (continued).

K	$S\ell_u(K)/S\ell_u(1)$	$I_{\max}(K)/I_{\max}(1)$ for							
		$\epsilon'(1)=0.1$	$\epsilon'(1)=0.3$	$\epsilon'(1)=0.5$	$\epsilon'(1)=0.7$	$\epsilon'(1)=0.9$	$\epsilon'(1)=0.95$	$\epsilon'(1)=0.99$	
24	0.0678	0.137	0.162	0.186	0.227	0.325	0.391	0.545	
25	0.0475	0.1004	0.119	0.138	0.169	0.244	0.296	0.419	
26	0.0328	0.0723	0.0868	0.100	0.123	0.180	0.219	0.314	
27	0.0224	0.0517	0.0618	0.0721	0.0889	0.131	0.160	0.231	
28	0.0151	0.0364	0.0442	0.0511	0.0632	0.0933	0.115	0.166	
29	0.0101	0.0257	0.0312	0.0359	0.0447	0.0623	0.0814	0.119	
30	0.0067	0.0177	0.0219	0.0252	0.0312	0.0462	0.0568	0.0831	

Table II. Representative numerical values of $A(K)/A(1)$ as a function of $\epsilon'(K=1)$ for the P_1 -branch, $(0;0)$ -band, $2\Sigma \rightarrow 2\Pi$ transitions of OH at 3000°K.

K	$A(K)/A(1)$ for			
	$\epsilon'(1) = 0.1$	$\epsilon'(1) = 0.5$	$\epsilon'(1) = 0.9$	$\epsilon'(1) = 0.95$
1	1.00	1.00	1.00	1.00
2	1.31	1.24	1.15	1.11
3	1.61	1.47	1.25	1.20
4	1.88	1.64	1.34	1.27
5	2.07	1.77	1.39	1.32
6	2.21	1.86	1.43	1.36
7	2.27	1.90	1.47	1.39
8	2.26	1.91	1.49	1.41
9	2.20	1.90	1.50	1.43
10	2.08	1.84	1.51	1.43
11	1.93	1.76	1.50	1.43
12	1.75	1.65	1.47	1.42
13	1.55	1.52	1.42	1.39
14	1.35	1.37	1.35	1.35
15	1.15	1.21	1.27	1.28
16	0.968	1.05	1.16	1.19
17	0.793	0.888	1.04	1.08
18	0.636	0.736	0.902	0.959
19	0.509	0.599	0.772	0.828
20	0.397	0.477	0.635	0.696
21	0.305	0.373	0.515	0.569
22	0.232	0.286	0.405	0.454
23	0.173	0.217	0.313	0.352
24	0.128	0.161	0.237	0.269
25	0.0935	0.119	0.176	0.201
26	0.0671	0.0859	0.129	0.147
27	0.0478	0.0615	0.0927	0.107
28	0.0335	0.0433	0.0657	0.0757
29	0.0236	0.0304	0.0463	0.0536
30	0.0161	0.0212	0.0321	0.0372

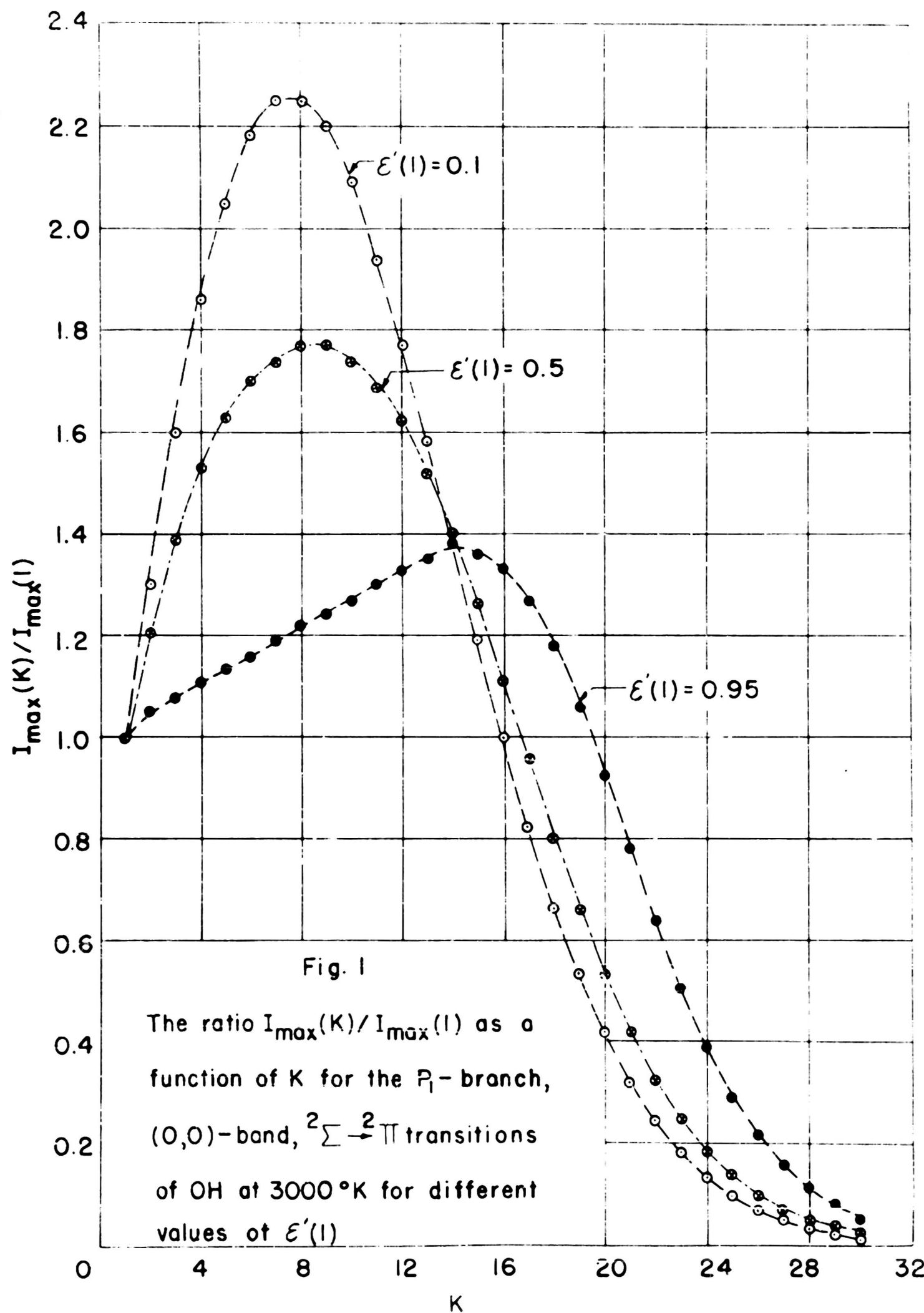


Fig. 1

The ratio $I_{\max}(K)/I_{\max}(l)$ as a function of K for the P_1 -branch, $(0,0)$ -band, $^2\Sigma \rightarrow ^2\Pi$ transitions of OH at 3000°K for different values of $\epsilon'(l)$

FIG. 2

THE RATIO $A(K)/A(1)$ AS A FUNCTION OF K FOR THE P_1 - BRANCH, $(0,0)$ - BAND, $^2\Sigma \rightarrow ^2\Pi$ TRANSITIONS OF OH AT 3000°K FOR DIFFERENT VALUES OF $\epsilon'(1)$

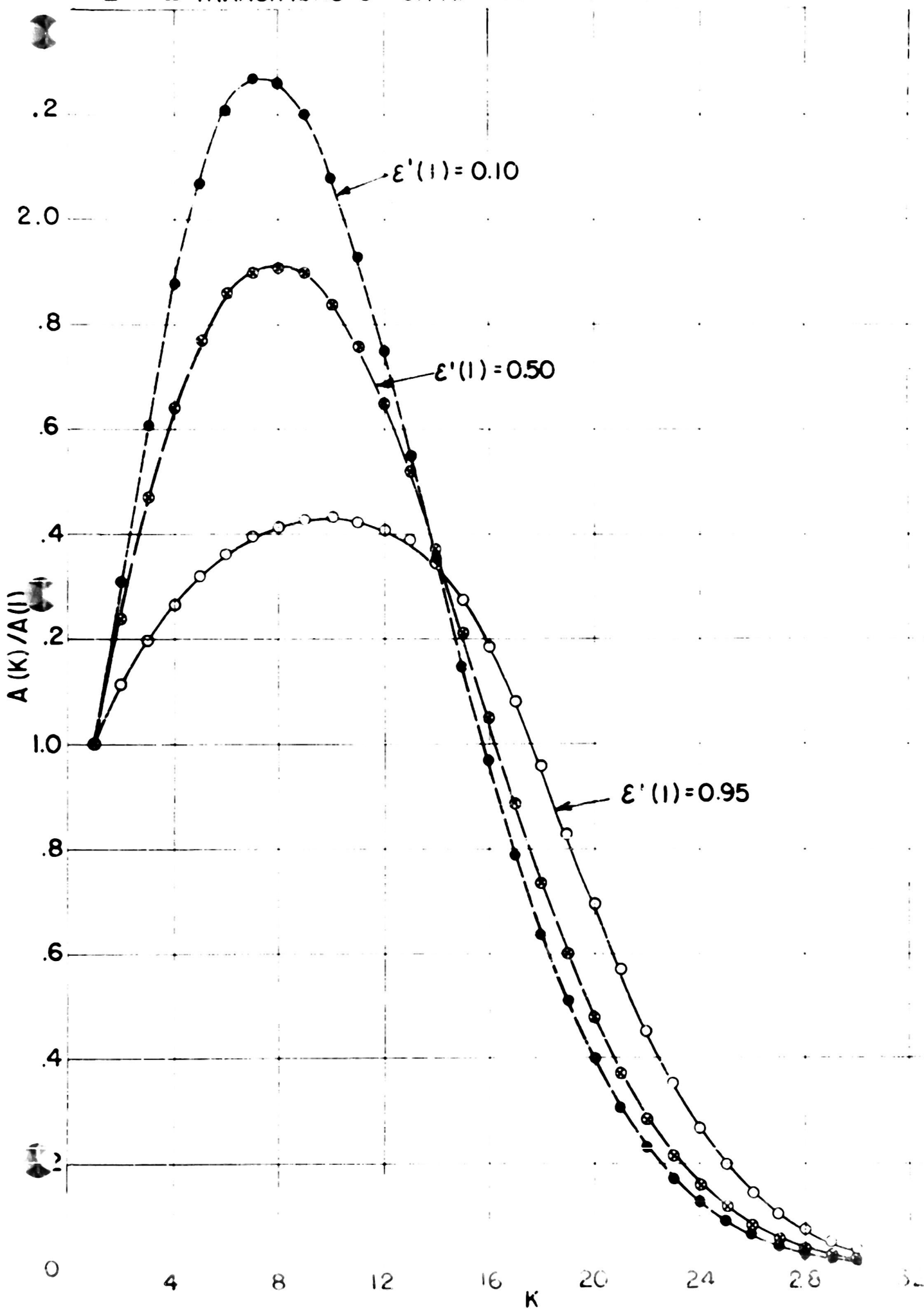


Fig. 3

Plot of $[E_u(K) - E_u(K')] \times 10^3, \text{cm}^{-1}$ vs. $\log \left\{ g_u(K) [q_{lu}(K)]^2 / g_u(K') [q_{lu}(K')]^2 \right\}$ for lines with equal peak intensities at 3000°K as a function of $\mathcal{E}'(l)$ for the P_1 -branch, $(O, O) - \text{band}, \Sigma \rightarrow \Sigma^2\Pi$ transitions of OH

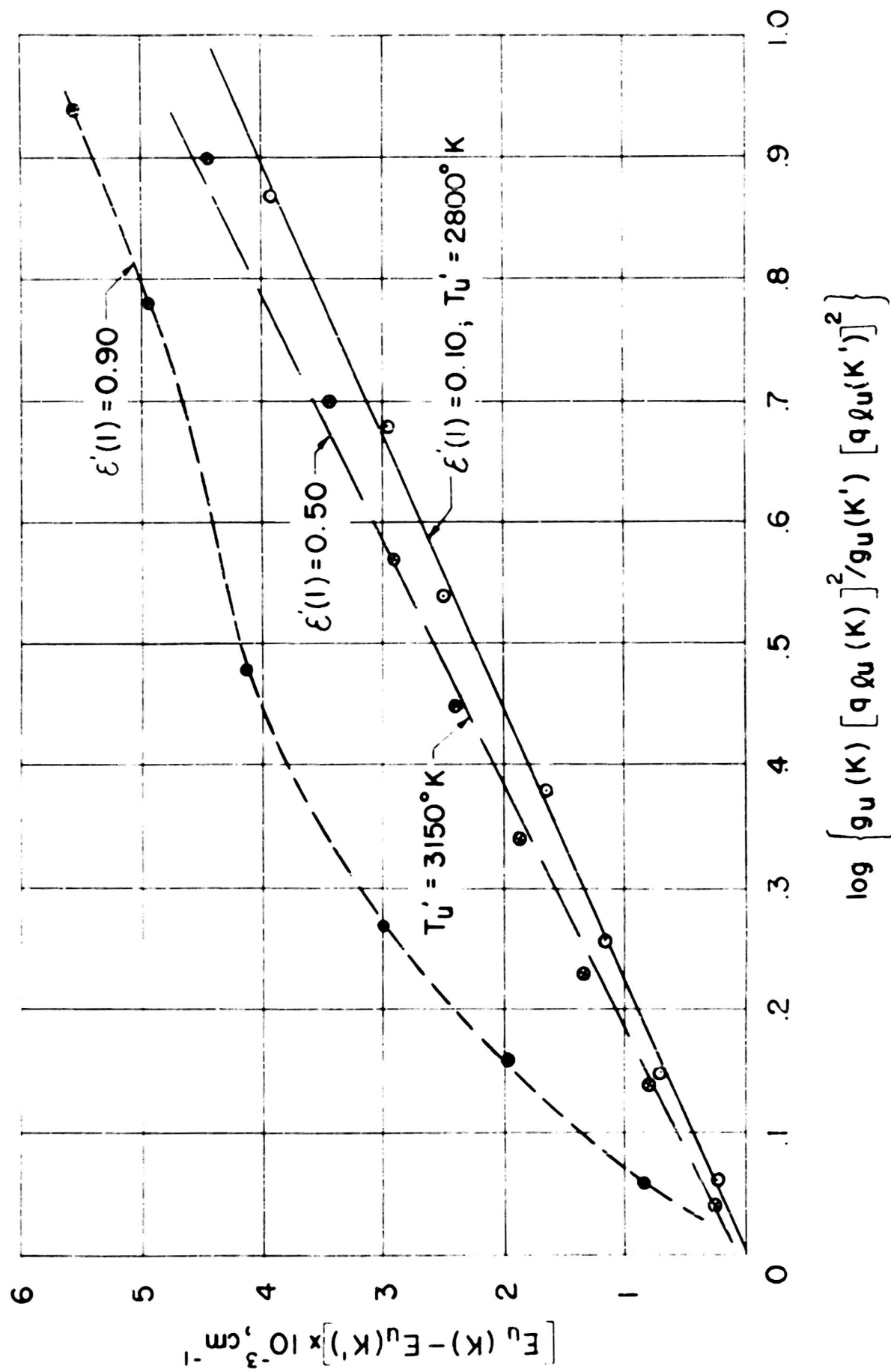
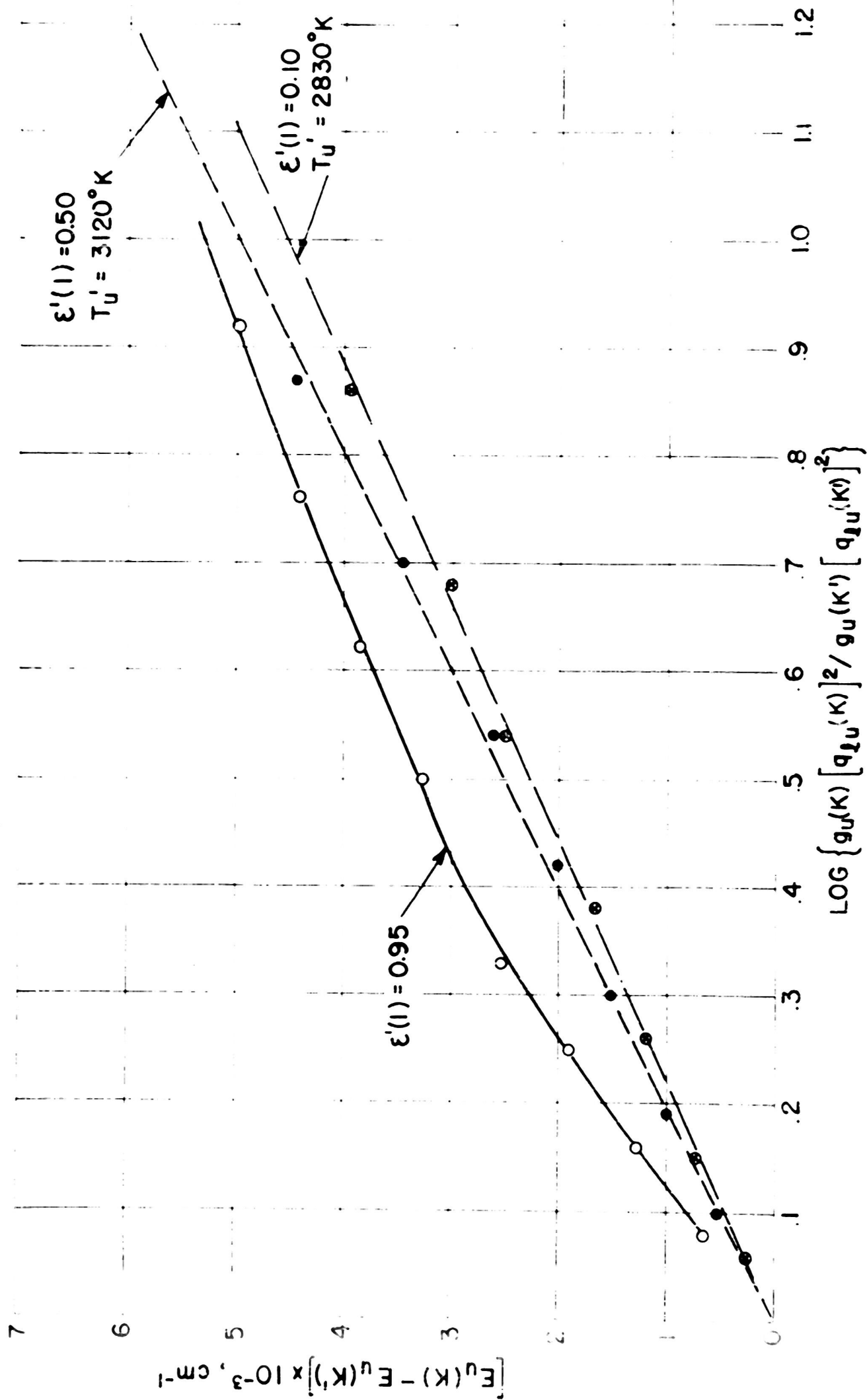


FIG. 4
 PLOT OF $[E_u(K) - E_u(K')] \times 10^{-3}, \text{cm}^{-1}$ vs. $\text{LOG} \left\{ g_u(K) [q_{lu}(K)]^2 / g_u(K') [q_{lu}(K')]^2 \right\}$ FOR LINES WITH EQUAL TOTAL INTENSITIES AT 3000°K AS A FUNCTION OF $\epsilon'(l)$ FOR THE P_1 -BRANCH, $(0,0) \rightarrow {}^2\Sigma \rightarrow {}^2\Pi$ TRANSITIONS OF OH.



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ADDENDUM TO TECHNICAL REPORT NO. 5
(to be added to Part IV, following p. 4)

LEGIBILITY PCOR

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IV. CONCLUDING REMARKS

In concluding the quantitative studies of the effect of self-absorption on apparent population temperatures in isothermal systems, it appears desirable to indicate the connection between this work and the interpretation of spectra obtained from flames. First of all, it must be acknowledged that flames are not isothermal emitters and that, therefore, any conclusions drawn from the study of isothermal systems can be applied to the interpretation of flame spectra only after it has been established that the flames under study constitute reasonable approximations to isothermal systems. In general, the distortion of experimental data resulting from temperature gradients in the field of view must also be considered. A quantitative study of the coupling between distortions resulting from self-absorption and from temperature gradients in the field of view is currently in progress.

The quantitative calculations described in the present analysis suggest that some of the reported "anomalies" concerning flame temperatures for OH cannot be accepted as valid experimental evidence without further quantitative proof. For example, a decrease in apparent population temperature from the bottom to the top of a flame may indicate either higher temperatures of OH or else higher concentrations of OH at the bottom of the flame. Similarly, "normal" temperatures for OH in $H_2 - O_2$ flames but "abnormal" temperatures in the same flames containing a trace of acetylene may indicate either chemiluminescence or else the initial production of large quantities of OH as the result of introduction of the acetylene. It may be possible to differentiate between these two alternative interpretations by performing absolute intensity measurements on flames. It is particularly disappointing, in this connection, to note the failure of the iso-intensity

methods, even for isothermal systems, to provide a definitive answer unless the extent of self-absorption is known to be small.

Attempts have been made to demonstrate the absence of self-absorption in flames by showing that absorption of light coming from a continuous source is weak. Studies of this sort are not convincing unless the experimental slit width is small compared to the width of the spectral lines under study. For the conditions which are usually employed in experimental studies on flames, the apparent integrated intensity of a spectral line could be smaller than the true value of the integrated intensity by several orders of magnitude. For this reason it is highly desirable to test for the absence of self-absorption by using as light source a radiator of the same spectral characteristics as the absorber under study. Weak absorption for continuous radiation and absence of self-absorption are not necessarily synonymous.

The preceding statements should not be interpreted to mean that the quantitative calculations demonstrate that anomalous population temperatures in flames are always the result of invalid interpretation of experimental data. Quite to the contrary, all of the anomalies may yet turn out to be real. However, it does appear to us that it would be highly desirable to consider anomalous flame temperatures as established only after every possible attempt has been made to eliminate distortion of experimental data by self-absorption or by temperature gradients in the light path. From the point of view of utilizing spectroscopic studies to obtain information concerning the mechanism of combustion reactions, the low-pressure flames of Gaydon and Wolfhard and of Gilbert appear to hold the greatest promise of yielding significant experimental data which can be interpreted in an unambiguous manner.